

# ELECTROCHEMICAL TECHNIQUE FOR TNT USING DISPOSABLE SCREEN-PRINTED ELECTRODES



Kim Rogers and Rebecca Pearson

U.S. Environmental Protection Agency  
National Exposure Research Laboratory-Las Vegas, NV 89193-3478

1

## Abstract

Screen-printed thick film electrodes are demonstrated as voltammetric sensors for measurement of 2,4,6-trinitrotoluene (TNT). The square wave voltammetric (SWV) scan technique was used to measure TNT in as little as 50  $\mu\text{L}$  sample volumes. This electrochemical assay was coupled with a solid phase extraction (SPE) protocol using 3M Empore SDB-RPS membranes. The explosive was extracted from the membrane using acetonitrile, which showed little effect on the assay at a final concentration of 10%. The coupling of SPE with SWV using disposable electrodes yielded a dynamic assay range of 2 ppb to 2 ppm for TNT. Potential interferences were examined for co-contaminants such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and breakdown products such as 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 1,3,5-trinitrobenzene, 2,4-dinitrotoluene, and p-dinitrobenzene.

2

## Introduction

Production, open-burn/detonation testing, and storage of explosive compounds (primarily 2,4,6-trinitrotoluene, TNT) has resulted in significant contamination of a number of munitions facilities throughout the U.S. Due to the mutagenic, toxic, and persistent nature of these compounds, their leaching into ground water and accumulation in the food chain has generated interest in the characterization and cleanup of contaminated sites as well as concern for human and ecosystem exposure. In response to the need for rapid and cost-effective field analytical methods for detection of these compounds, rapid screening assays based on chemical, immunochemical and electrochemical techniques have been recently reported [1,2]. Although each of these techniques can perform relatively rapid analyses, each method shows limitations in areas such as instrument cost, consumable cost, selectivity or sensitivity. Among these methods, one of the promising techniques uses square wave voltammetry in combination with disposable screen printed electrodes [3]. This project will demonstrate improved detection limits for this technique.

3

## Summary

TNT was analyzed by SWV using disposable electrodes. Sample volumes as small as 50  $\mu\text{L}$  were analyzed in as little as 10 s. Direct sample analysis yielded a linear response up to 2 ppm with a detection limit of 200 ppb.

The use of a SPE protocol added about 40 min to the assay time and lowered the detection limit for TNT to 2 ppb.

Interferences resulting from RDX co-contamination could be removed in laboratory standards by acidification of the sample prior to analysis.

Breakdown products typically found in explosives contaminated samples did not interfere with laboratory analysis of TNT. Nevertheless, for environmental samples in which breakdown product concentrations can exceed those of their parent compounds, significant interference would be expected.

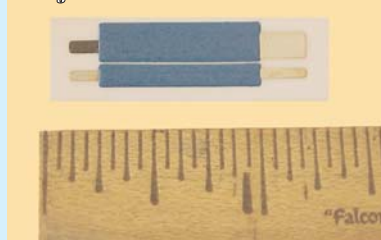
The speed, simplicity, cost-effectiveness and sensitivity of this assay make it an excellent candidate for development as a field analytical method.

4

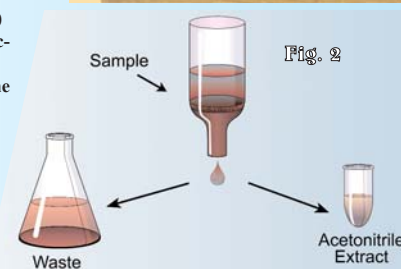
## Experimental Methods

**Figure 1** Square wave voltammograms were obtained using a CHI 620 Electrochemical Analyzer. Disposable electrodes were obtained from Dr. J. Wang (New Mexico State University, Las Cruces, NM). The electrode strips were 1 mm x 2.5 cm printed on a ceramic substrate that was 1 cm x 3 cm. The electrodes consisted of silver ink for the reference/counter electrode and carbon ink for the working electrode. Dielectric separated the leads from the working portion of the electrodes. For TNT standards, voltammograms were obtained for 50  $\mu\text{L}$  samples in phosphate buffered saline, PBS ( $\text{Na}_2\text{HPO}_4$ , 10 mM; NaCl, 100 mM; pH 7.4) containing 10% acetonitrile and 0-3000 ppb TNT. Stock solutions of breakdown products were analyzed in a similar manner but included the addition of HCl (10 mM). Possible TNT breakdown products included 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, 1,3,5-trinitrobenzene, 2,4-dinitrotoluene, p-dinitrobenzene.

Fig. 1



**Figure 2** For extraction of TNT, standards (2-50 ppb solutions) were passed through solid phase extraction (SPE) membranes (3M Empore / SDB-RPS extraction cartridges). TNT was re-extracted from the membrane with 300  $\mu\text{L}$  of acetonitrile, the solution concentrated by evaporation to 100  $\mu\text{L}$ , and 50  $\mu\text{L}$  analyzed by SWV.



## Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded this research and approved the abstract as a basis for presentation. The actual poster has not been peer reviewed by EPA.

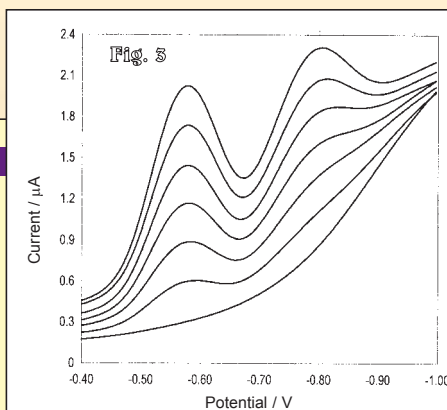
## References

- Jenkins, T.; Thorne, P.; Walsh, M. Field Screening Method for TNT and RDX in Groundwater, 1994, U.S. Army Corps of Engineers, CRREL, Report 9-14.
- Craig, H.; Ferguson, G.; Markos, A.; Kusterbeck, A.; Shriver-Lake, L.; Jenkins, T.; Thorne, P. Field Demonstration of On-Site Analytical Methods for TNT and RDX in Ground Water, 1996, Proceedings of the Rocky Mountain Hazardous Substances Research Center, Manhattan, KS.
- Wang, J.; Lu, F.; Macdonald, D.; Lu, J.; Ozsoz, M.; Rogers, K. *Talanta* 1998, 46, 1405-1412.

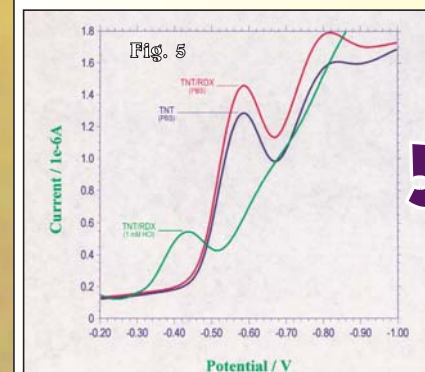
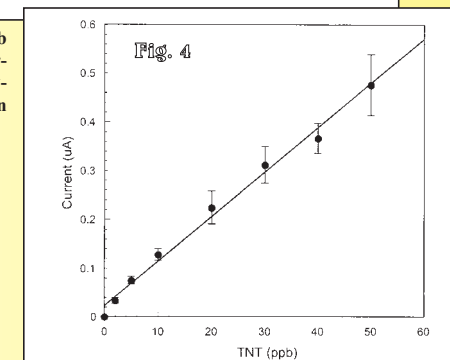
5A

## Results

**Figure 3** shows square wave voltammograms for increasing concentrations of TNT using screen-printed carbon electrodes. The peak response was linear for TNT throughout the concentration range tested. Sample volumes of 50  $\mu\text{L}$  were analyzed in 10 s using this technique. The detection limit for the direct analysis of TNT in water samples was 0.2 ppm.



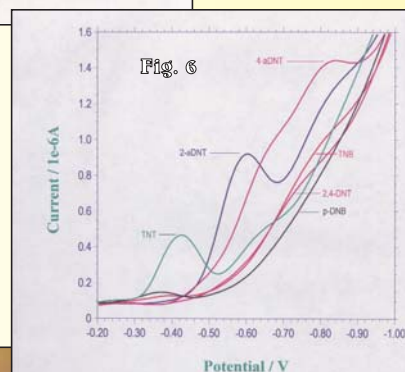
**Figure 4** The detection limit for TNT using the direct assay procedure was significantly improved by adding a solid phase extraction (SPE) protocol. The explosive was extracted from the membrane using acetonitrile. After concentration by evaporation, the acetonitrile extract was diluted 1:10 into PBS and 50  $\mu\text{L}$  was applied directly to the electrode. TNT measured using the SPE procedure also yielded a linear calibration plot with a dynamic range from 2 ppb to 50 ppb (Fig. 4). Percent recoveries calculated from the electrode ranged between 30 and 45 percent. Recovery of the TNT was higher at the lower concentrations. Although the recoveries were less than optimal, the concentration factor of 1:500 yielded an increase in sensitivity of 100 fold.



5B

## Results continued

**Figure 5** The two major explosive contaminants found in environmental samples are TNT and RDX. Voltammograms shown here are: TNT, 2 ppm, in PBS at pH 7.4; TNT + RDX, both at 2 ppm, in PBS at pH 7.4; TNT + RDX, both at 2 ppm in 10 mM HCl. Although the reduction peak potential for RDX is significantly more negative than the first reduction peak for TNT, the presence of RDX increases the apparent current for TNT. The acidification of the sample eliminates the RDX signal so that the resulting signal for mixture of TNT and RDX is due only to TNT.



**Figure 6** To determine the possible interferences resulting from explosive breakdown products, several related compounds (primarily breakdown products of TNT) were analyzed. Figure 6 shows overlaid voltammograms of TNT and selected breakdown products at 2 ppm (acidified; see Fig. 5). The following abbreviations appear in the figure: 2-amino-4,6-dinitrotoluene (2-aDNT), 4-amino-2,6-dinitrotoluene (4-aDNT), 1,3,5-trinitrobenzene (TNB), 2,4-dinitrotoluene (2,4-DNT), p-dinitrobenzene (p-DNB). With the exception of 2-amino-4,6-dinitrotoluene, there appears to be little interference at the TNT peak potential.